# Photoenhanced Toxicity of Oil to Larval Fish

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# Phototoxicity

**n. an adverse reaction to ultraviolet light (UV) caused by chemicals**

**<u>Photoenhanced toxicity of oil:</u>**

**Increase in petroleum toxicity under natural sunlight or lab UV compared to effects observed with minimal UV**

# Introduction

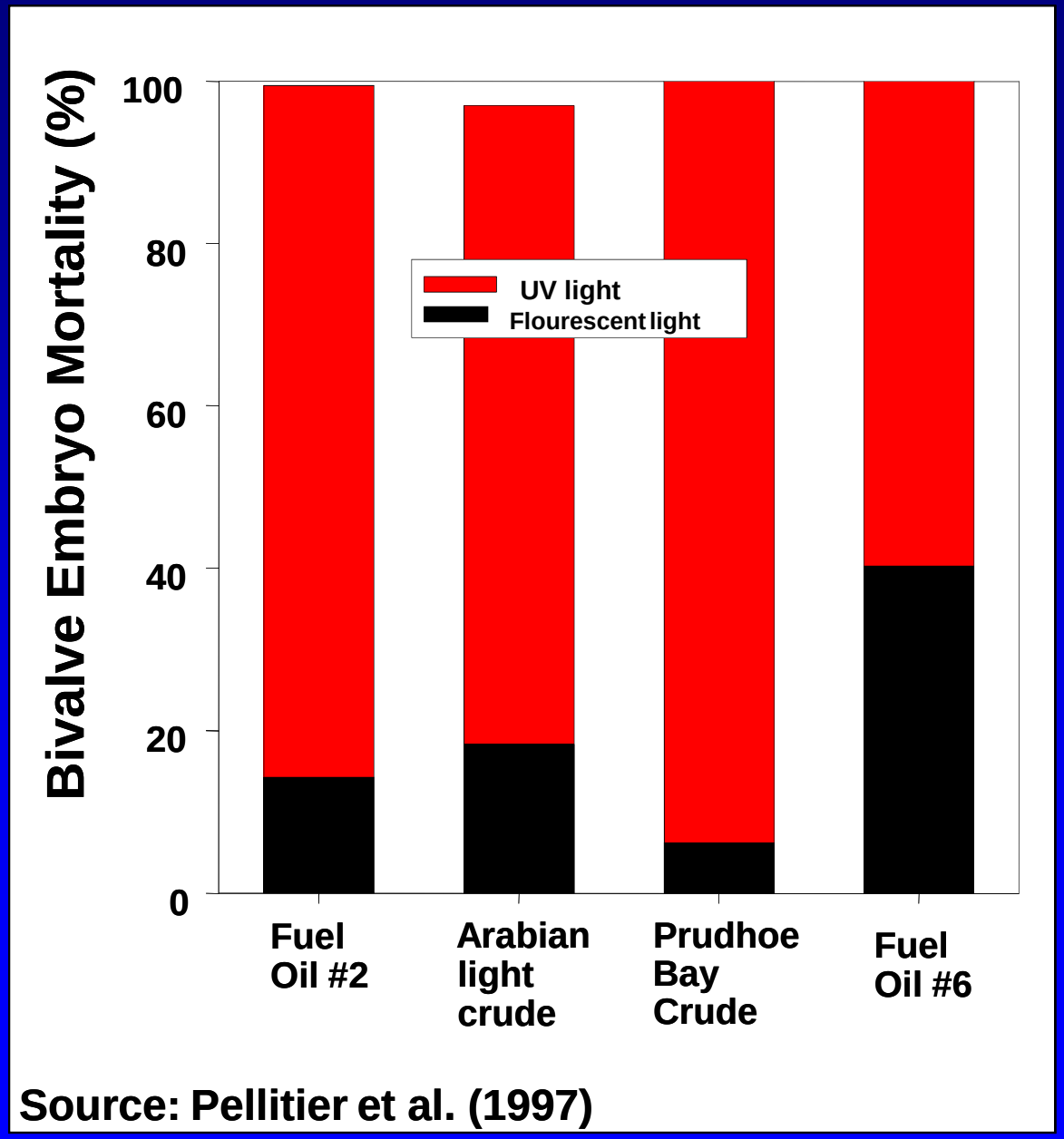
**Petroleum is phototoxic:**

* fresh and weathered oils and oil products
* 2 to >100 fold increase in toxicity

**Inadequate consideration of phototoxicity in oil spill response and impact assessment:**

* majority of tox and bioassays data conducted under fluorescent lighting
* tests do not have ecologically relevant levels of UV

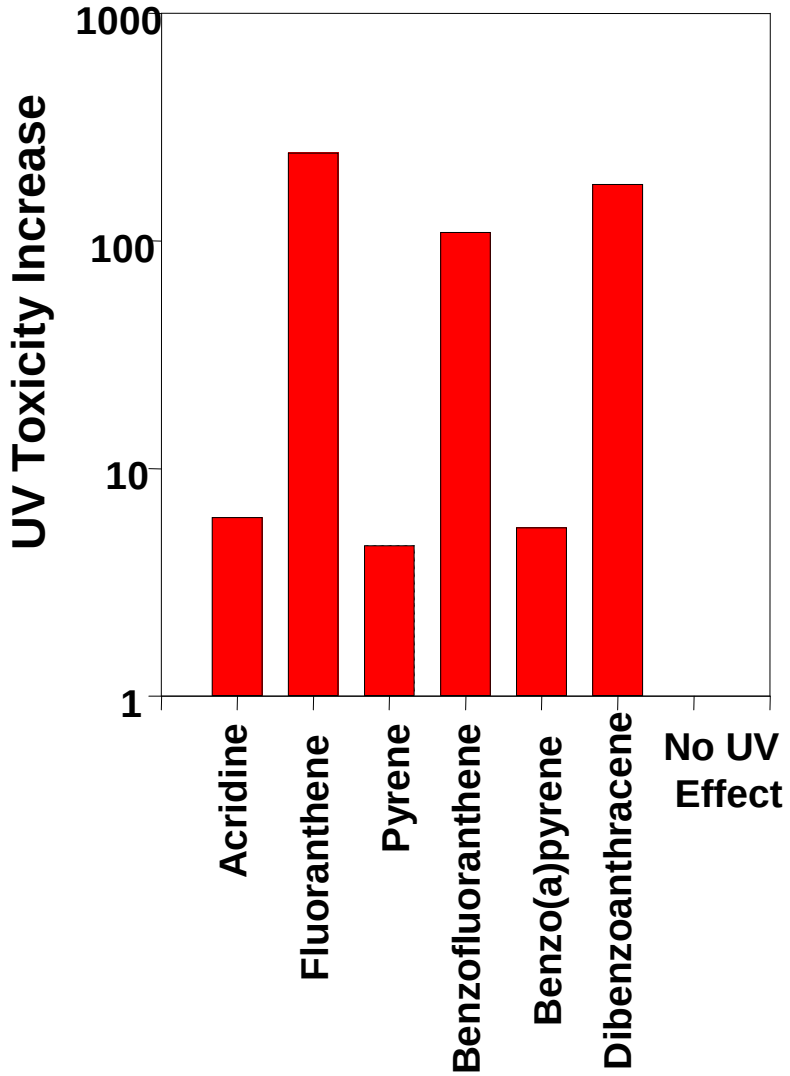
# Oil is more toxic with UV



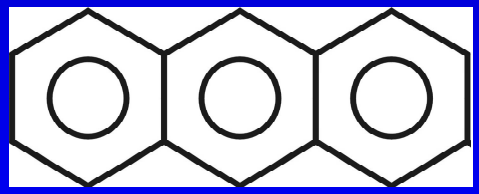

Source: Pellitier et al. (1997)

- fresh, weathered oils
- crudes, middle distlillates, heavy fuel oils
- chemically dispersed oil

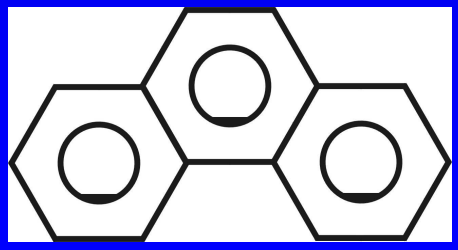
# PAH composition determines phototoxicity




- specific PAHs and heterocyclic aromatics
- 3 to 5 rings, specific conformations
- limited effect of alkyl substitution
- PAH absorbance spectrum



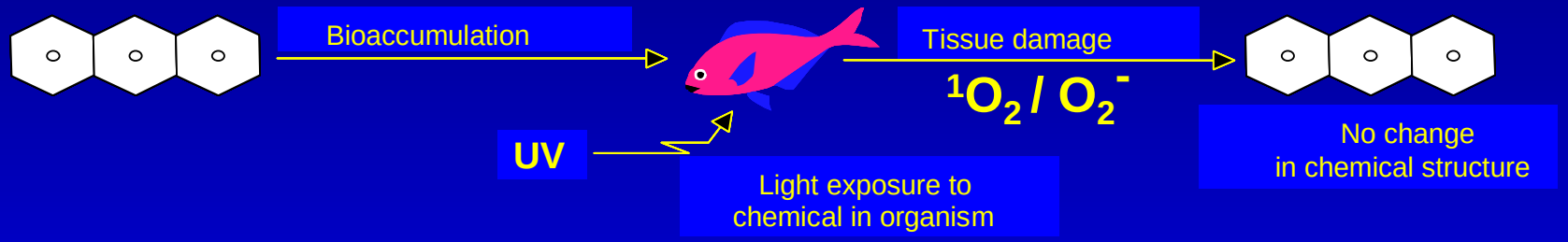
**anthracene (>100x phototoxic)**



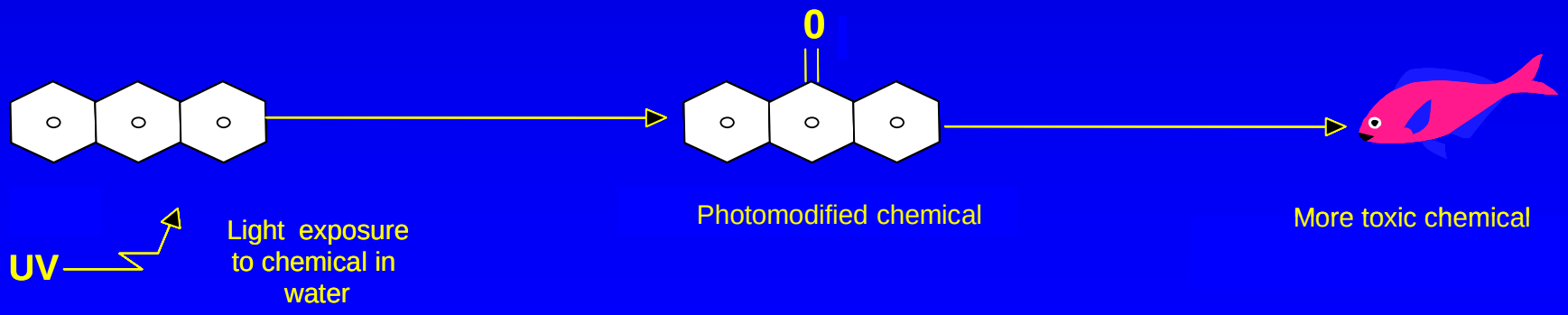
**phenanthrene**

# Mechanisms of Phototoxicity

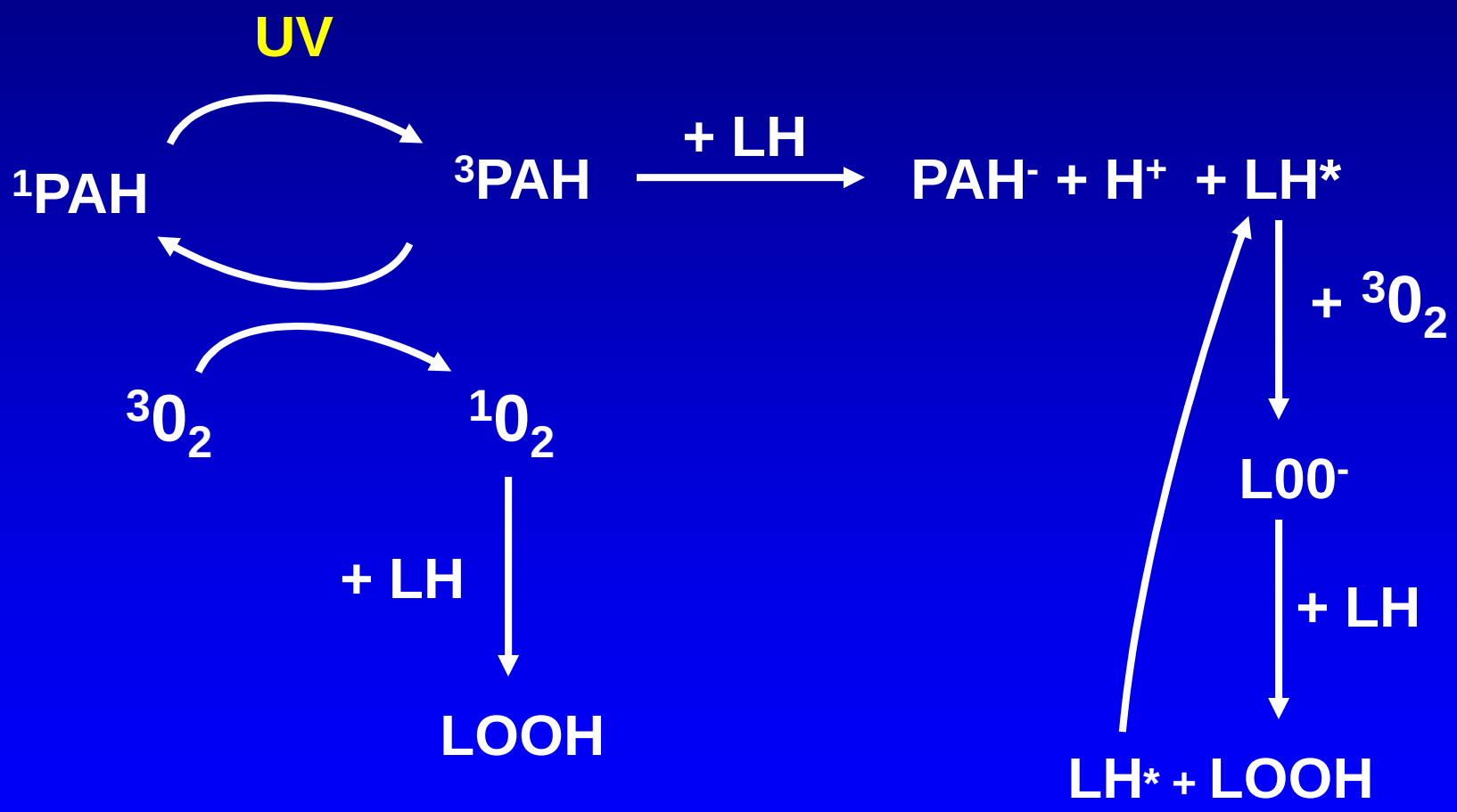
Photosensitization:
Chemical absorbs and releases light energy



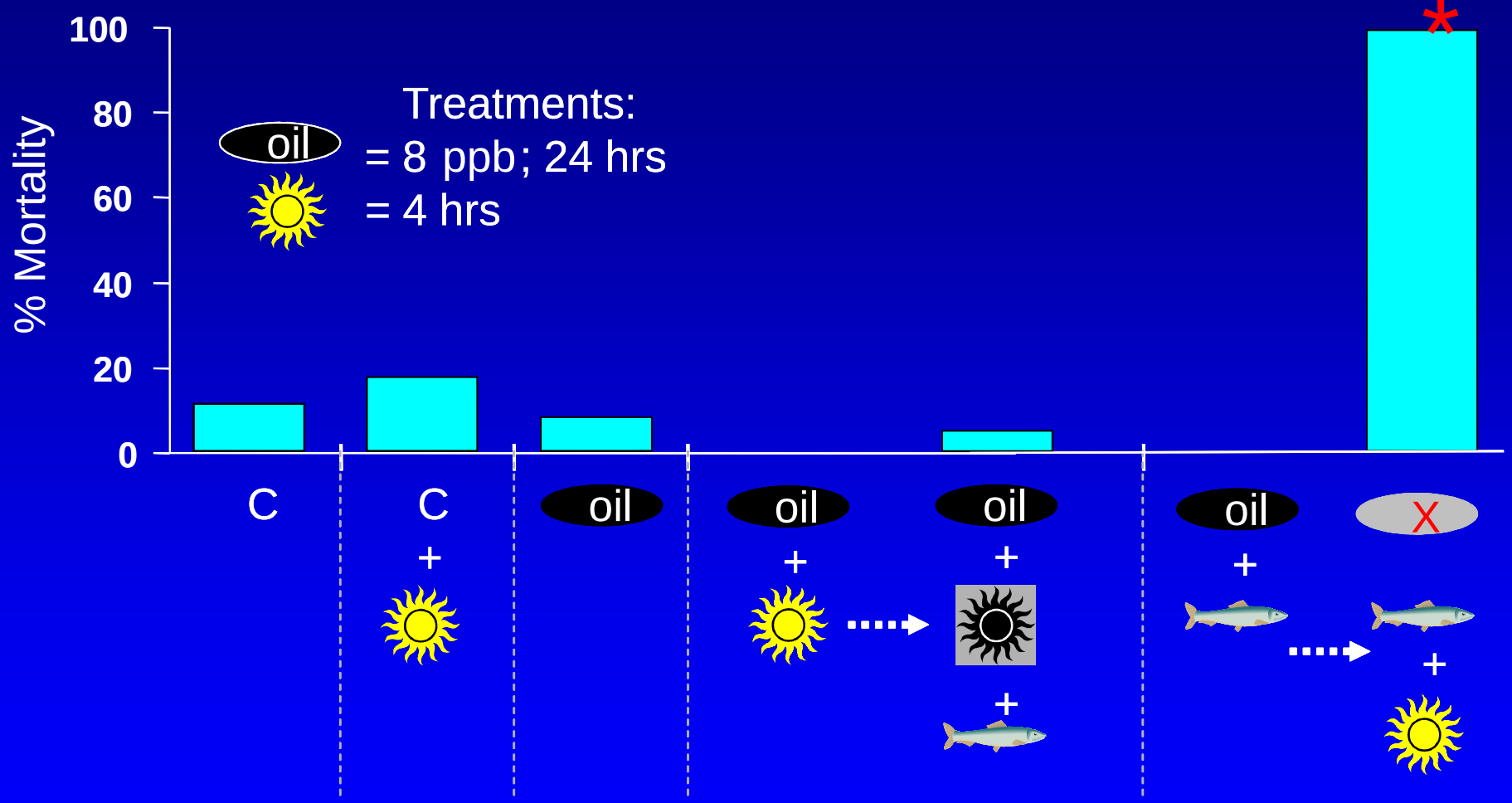

Photomodification:
Chemical transformed to more toxic product



# Photosensitization Reactions



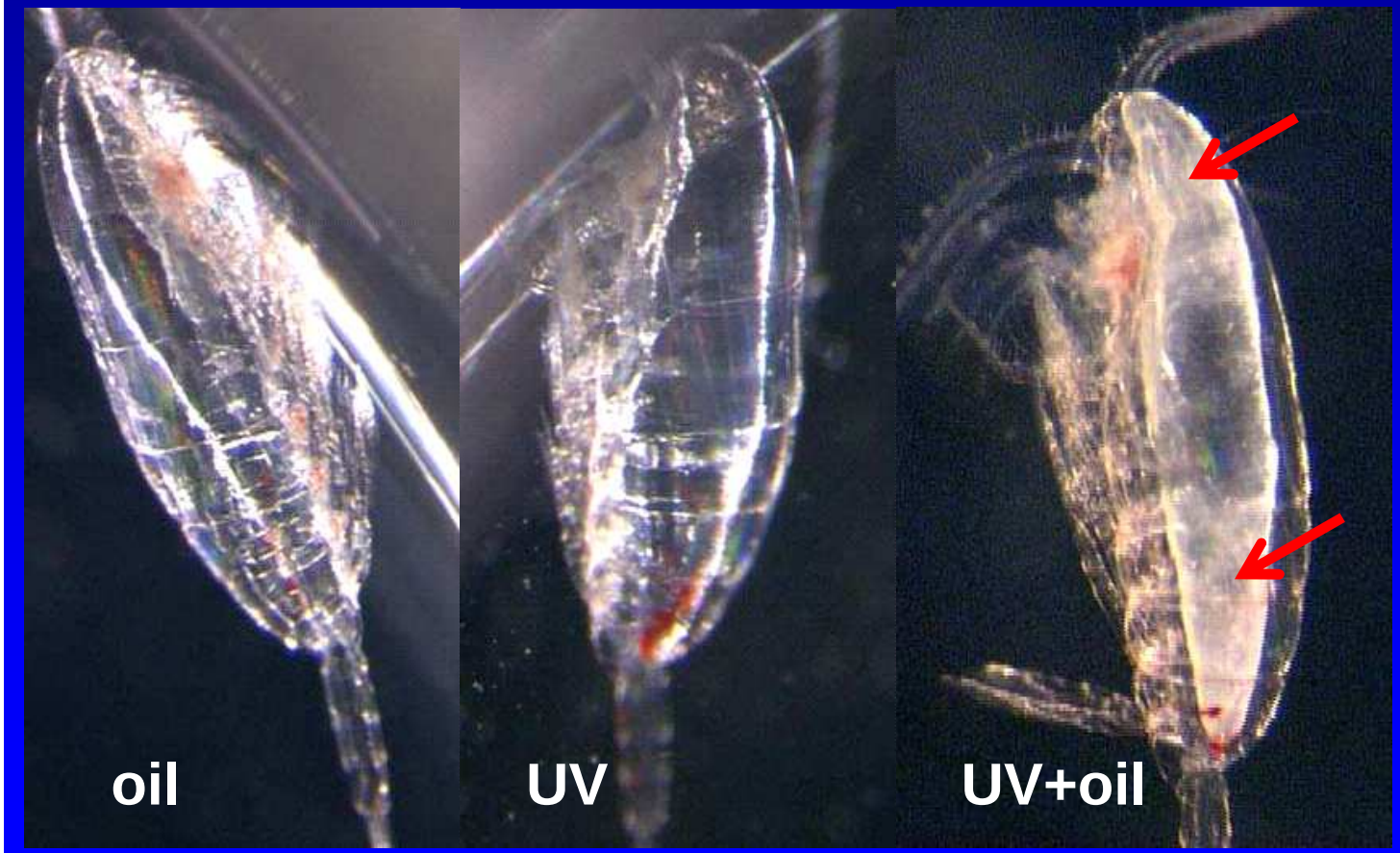
# Photosensitization:
# UV increases toxicity in herring larvae pre-exposed to oil




Source: Barron et al. 2003. ETC 22:650

# Alaska North Slope crude oil phototoxicity to marine zooplankton

- Field collected calanoid copepods
- 2 ug/L tPAH 24 hr exposure; 4 to 8 hr low UV



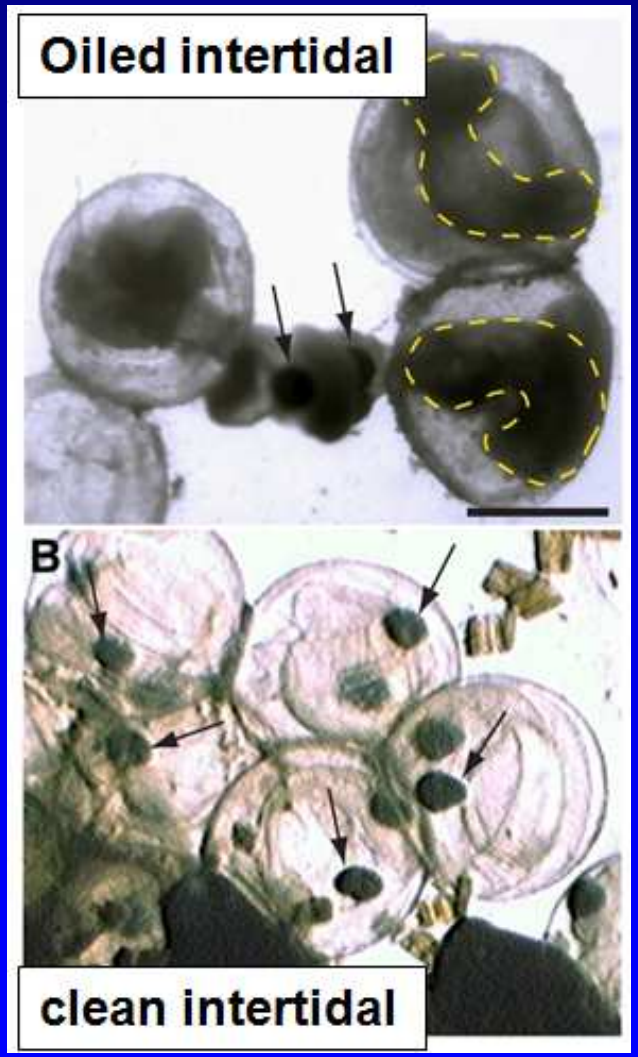

**UV+oil :**

- Indications of lipid sac peroxidation
- death, immobility, impaired swimming

Source: Deusterloh et al 2002. EST 36:3953

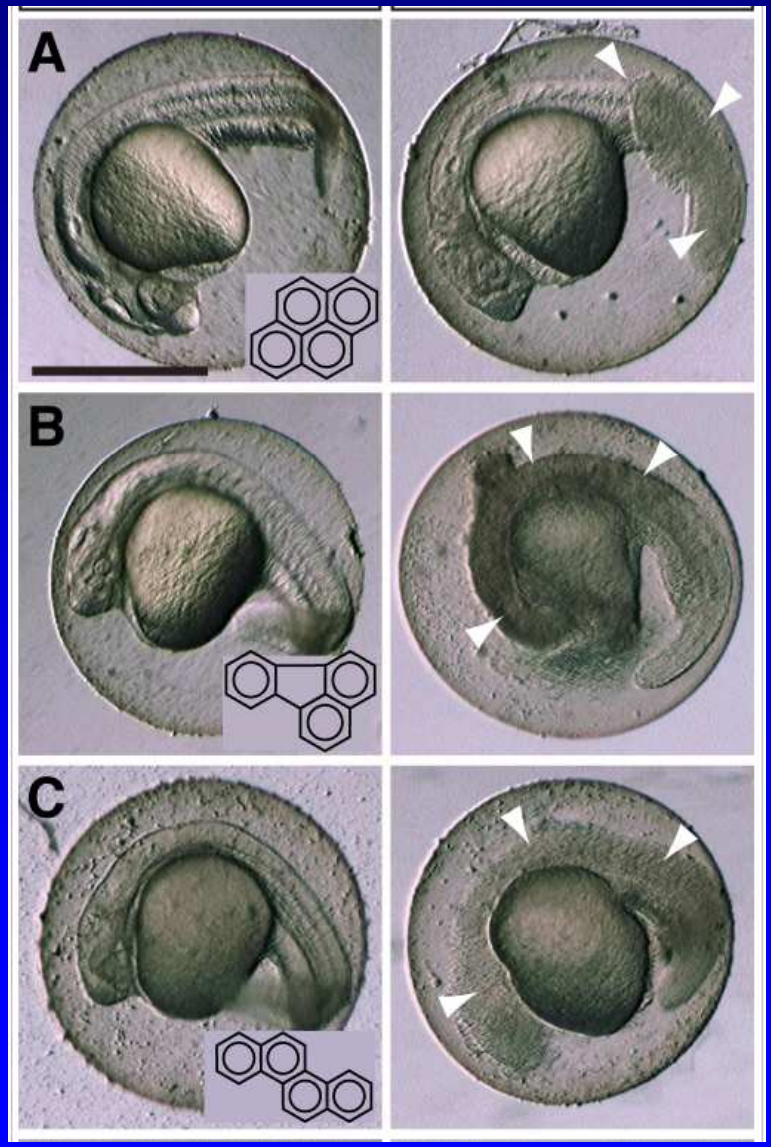
# Separate etiology than oil-only exposure

Bunker oil field exposure




**Oil+UV**
**herring embryo tissue necrosis**

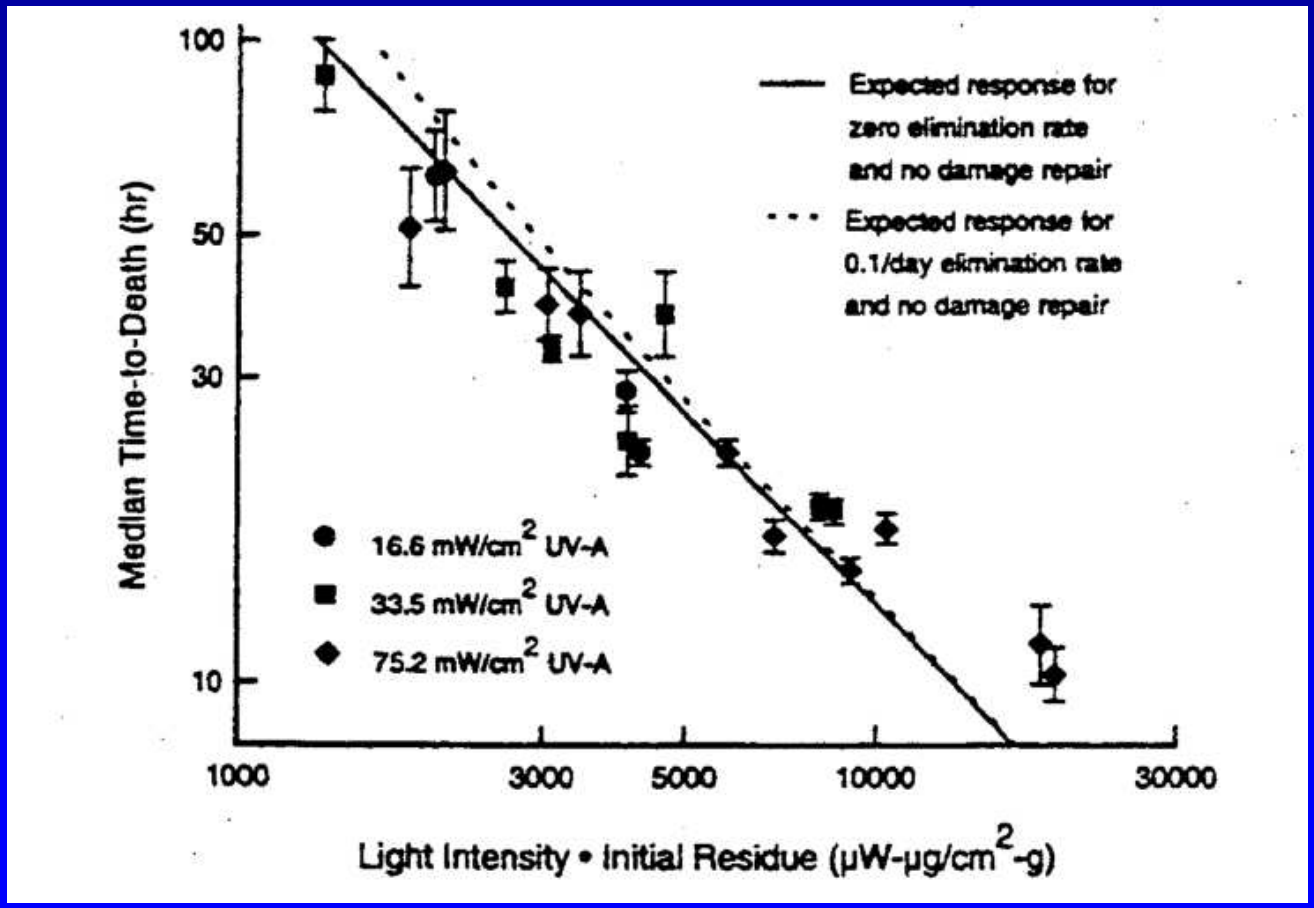
single PAH lab tests




**Source: Incardona et al 2012. PLoS One 7:e30116**

# Reciprocity Relationship

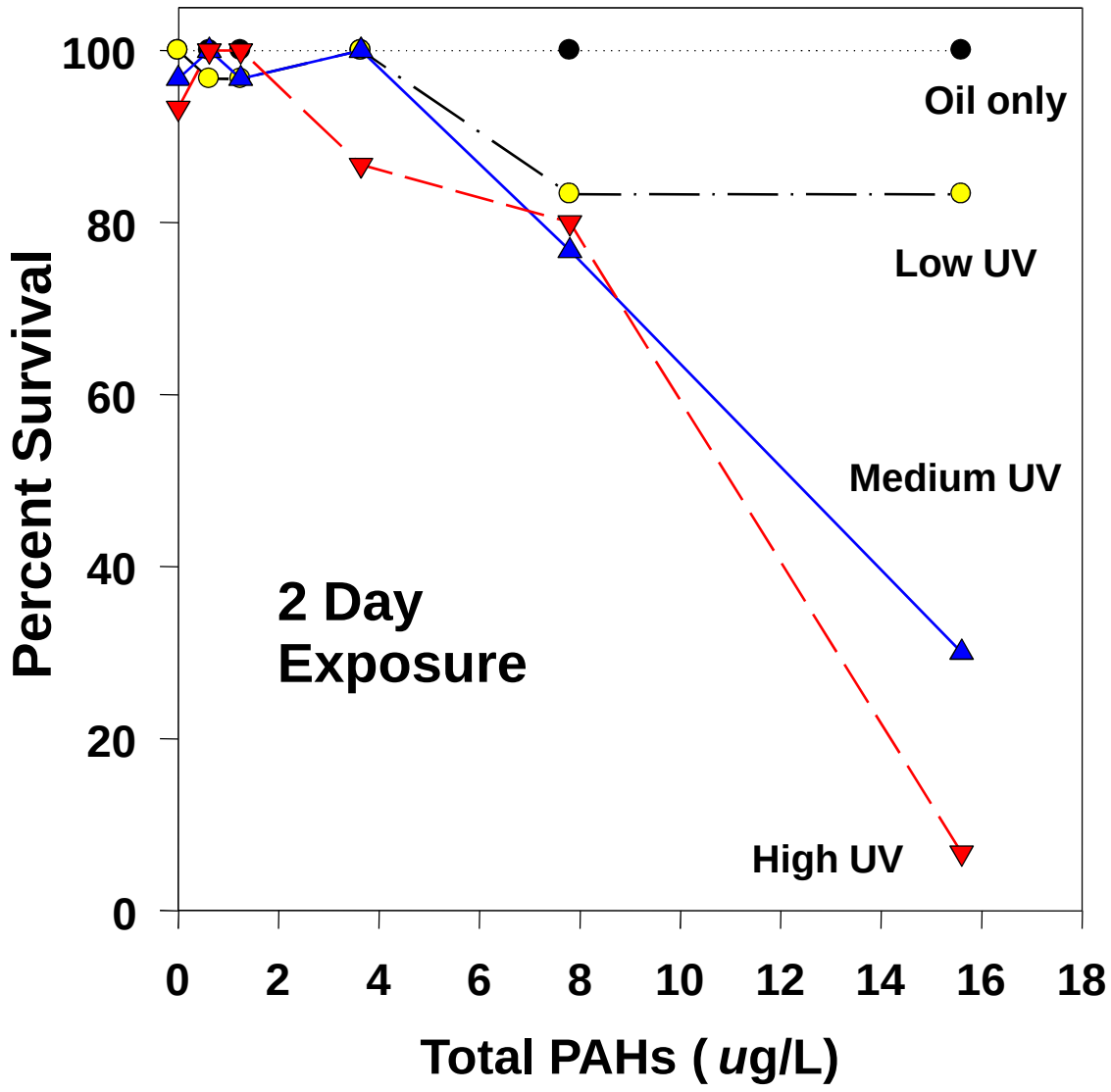
## Phototoxicity = *f* (UV x PAH)




**UVA important driver of toxicity**

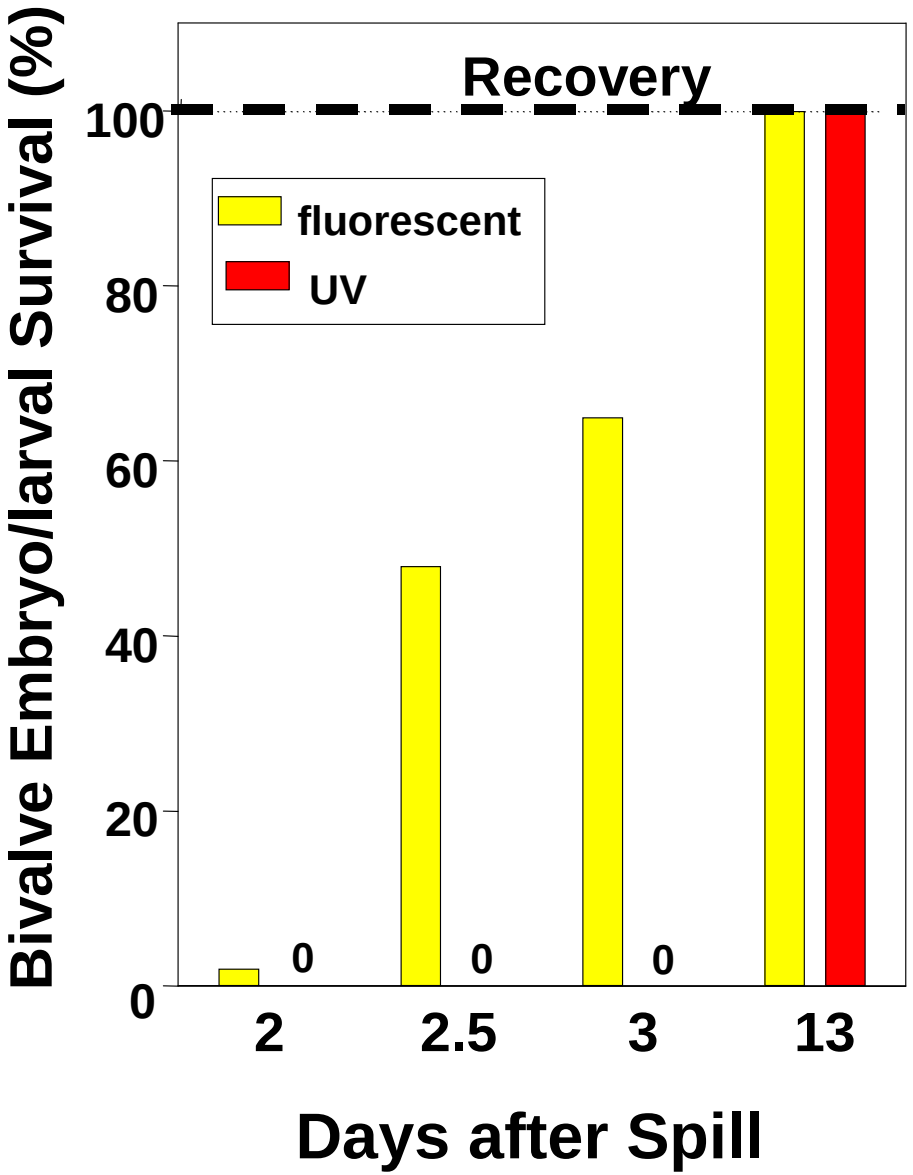
***Source: Ankley et al. 1995. ES&T 29:2828***

# UV and oil dose-response




Source: Little et al. 2000. ETC 19:926

- weathered middle distillate
- larval silversides

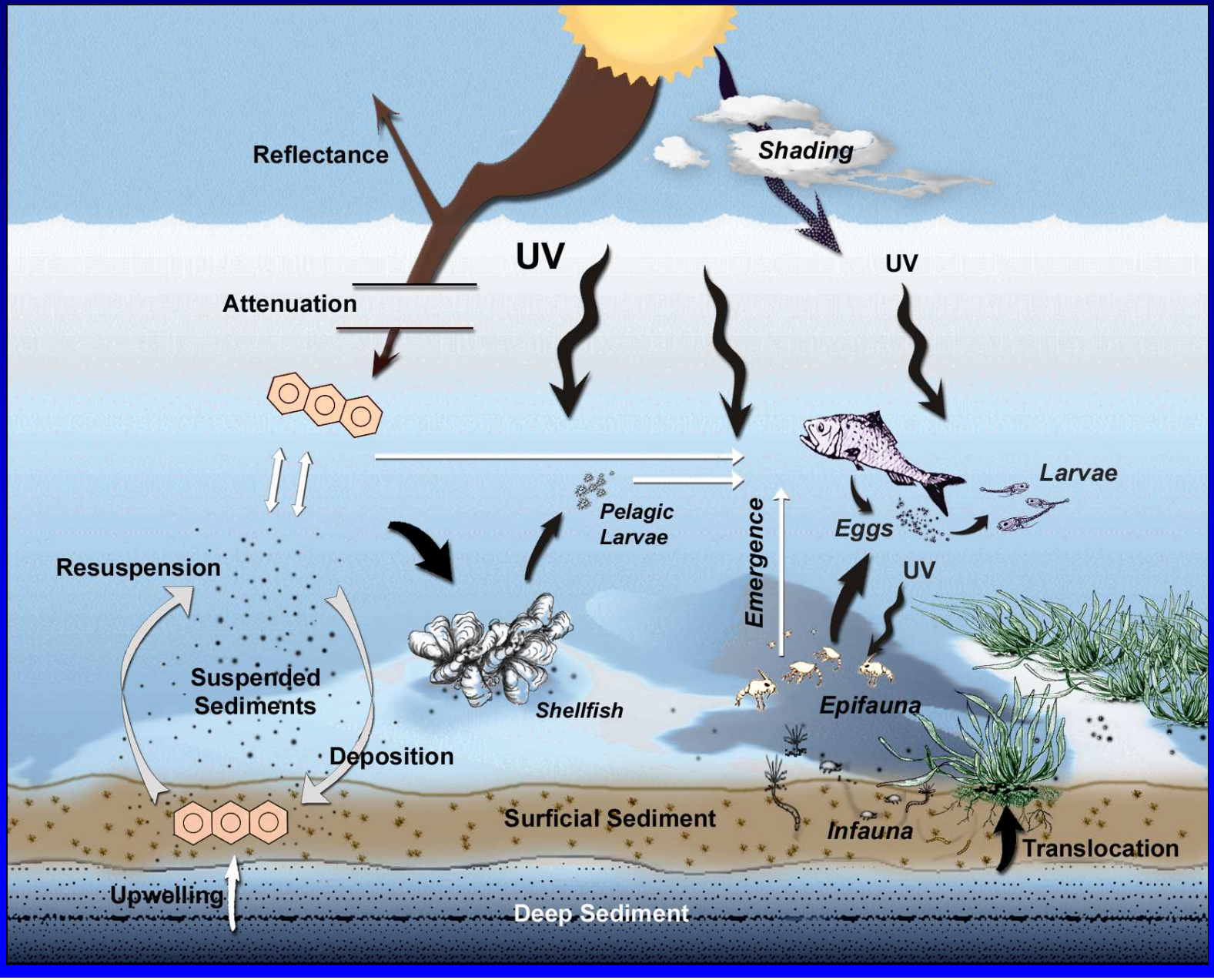



*Source: Ho et al. (1999)*

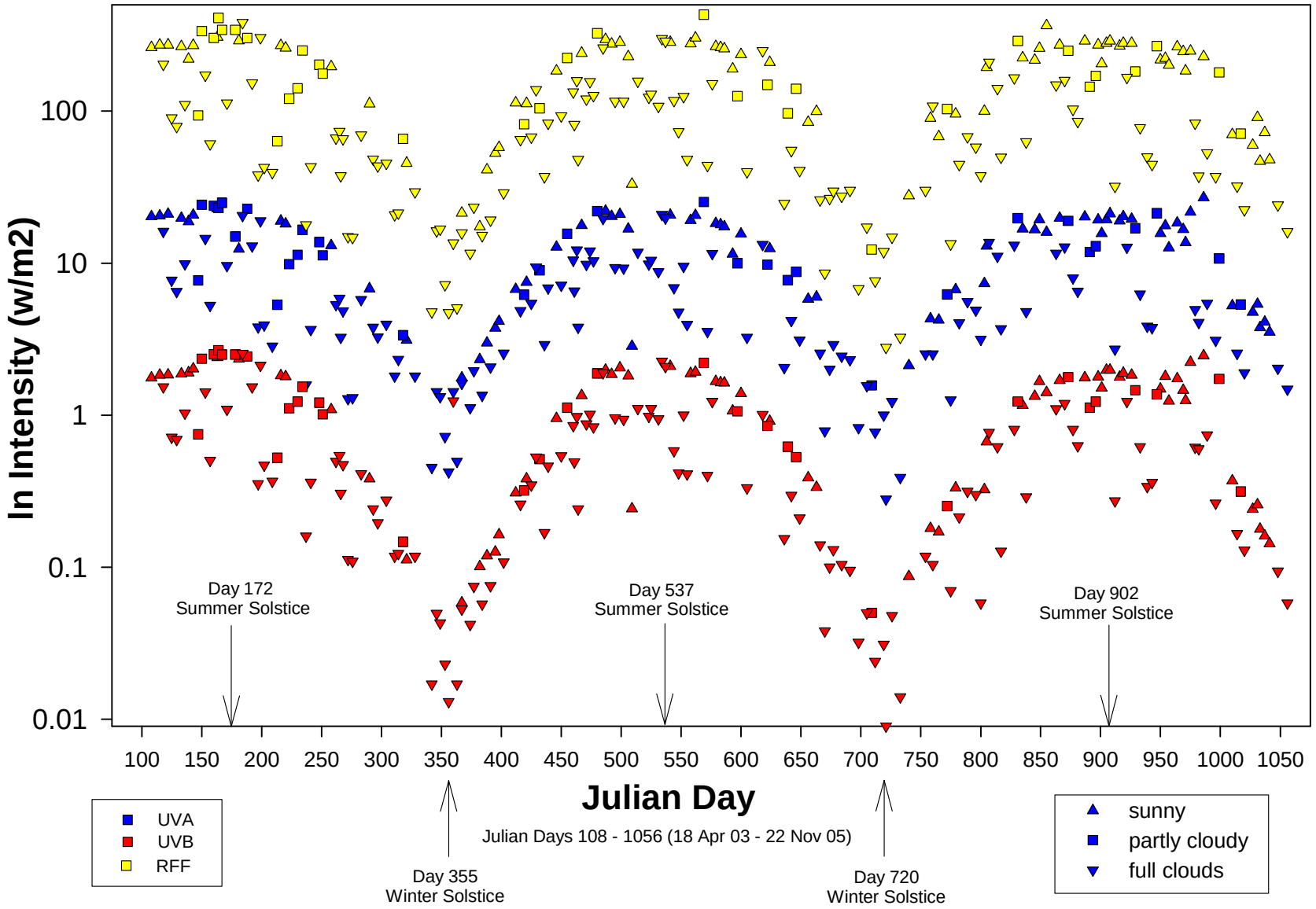
# Photoenhanced Toxicity of North Cape Oil Spill Water (Fuel oil #2)

- Lab tests of field collected spill water

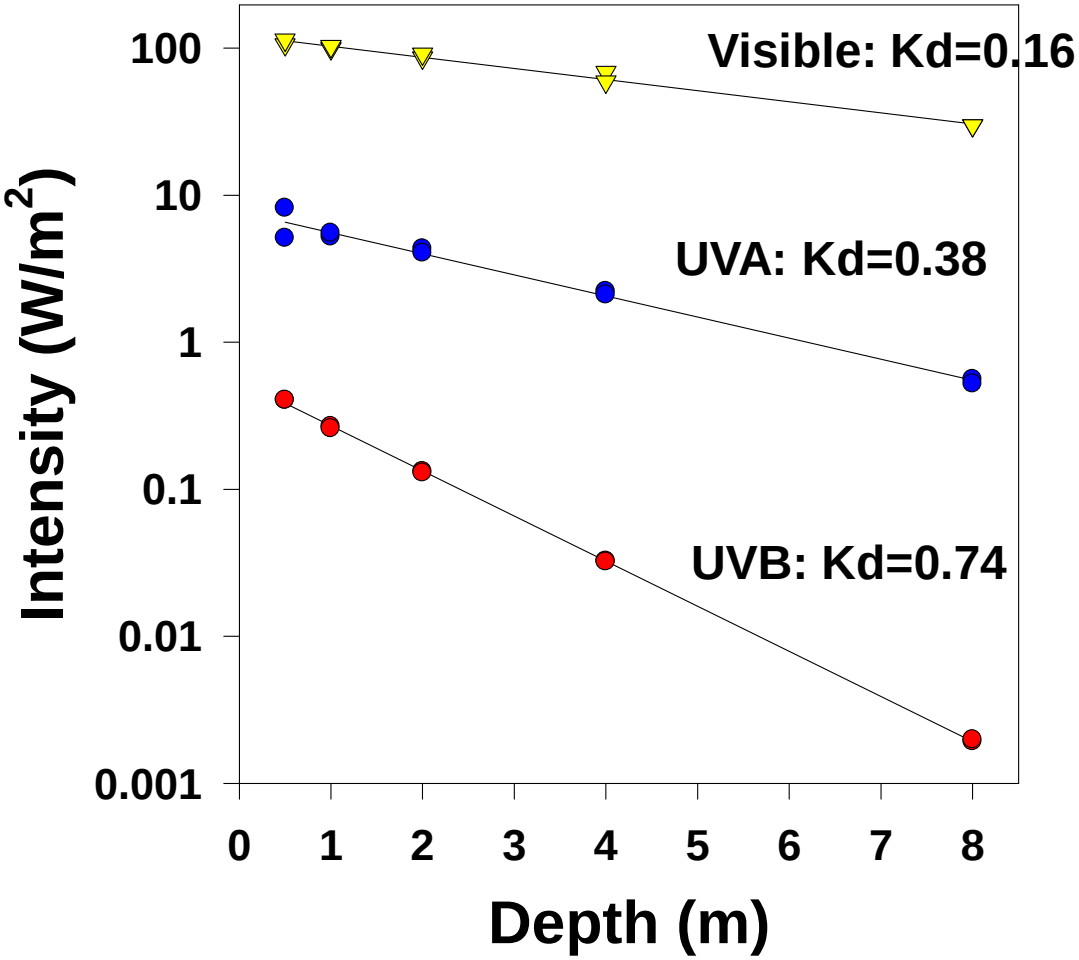
# UV exposure affected by sunlight intensity, photoperiod, attenuation



# Incident sunlight, Valdez Alaska (61.1231°N, 146.3053°W )



# Water column attenuation and Kd




**Kd:** slope of Ln intensity vs depth

- larger values: > attenuation; less clarity

90% attenuation depth:
$Z_{90} = 1/Kd$
(eg, 0.5 kd: 2 m $Z_{90}$)

# PWS, Alaska: June Attenuation Coefficients

40 km

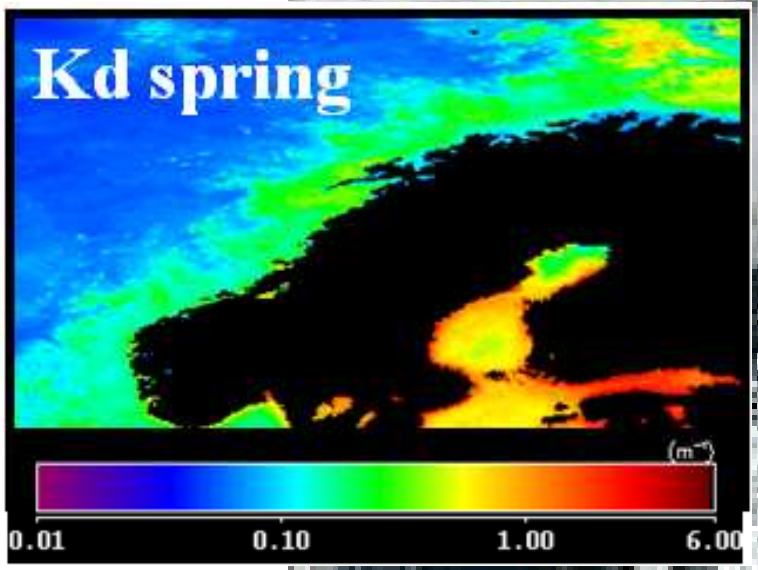
Vis Kd

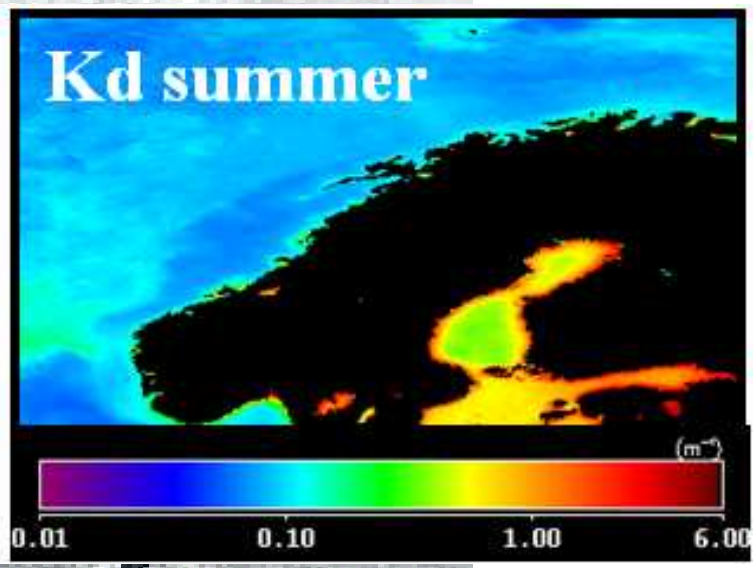
>2

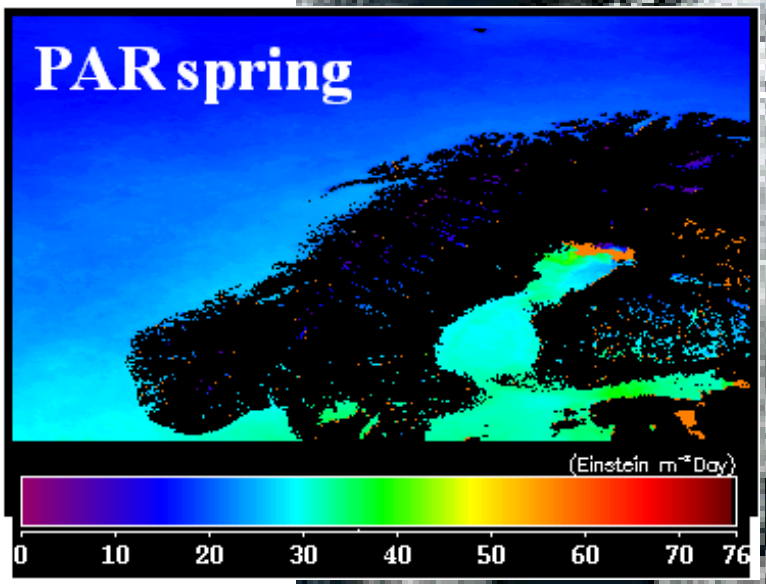
0.5 - 1

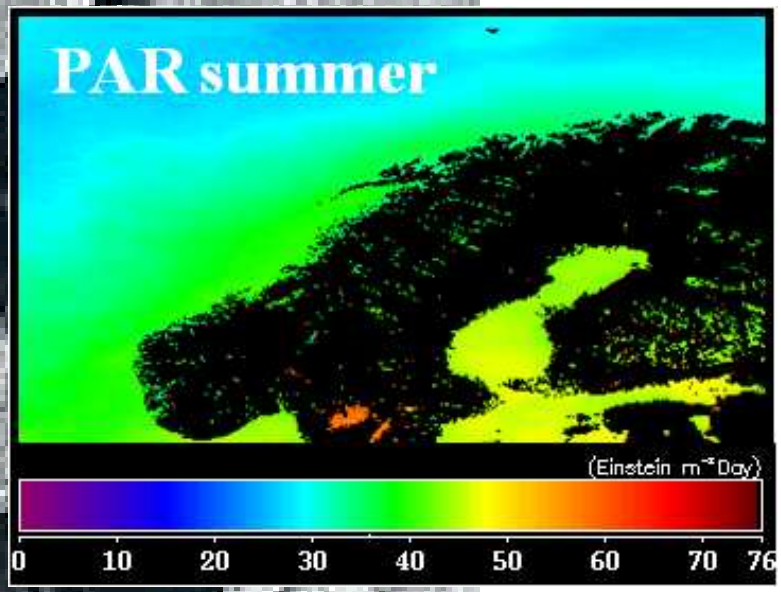
0.1 – 0.3

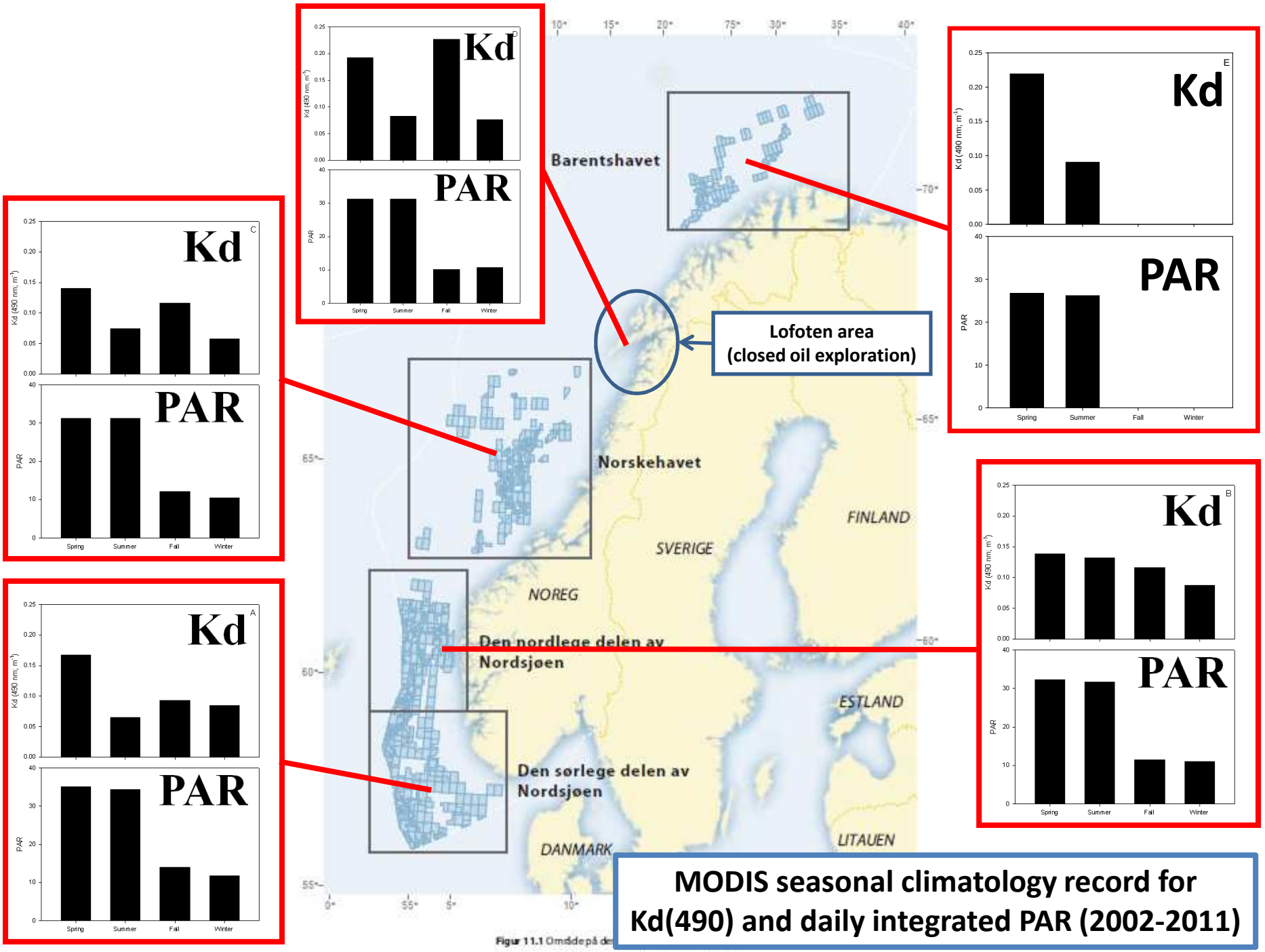
# MODIS seasonal climatology record for Kd(490) and daily integrated PAR (2002-2011)






**MODIS seasonal climatology record for Kd(490) and daily integrated PAR (2002-2011)**

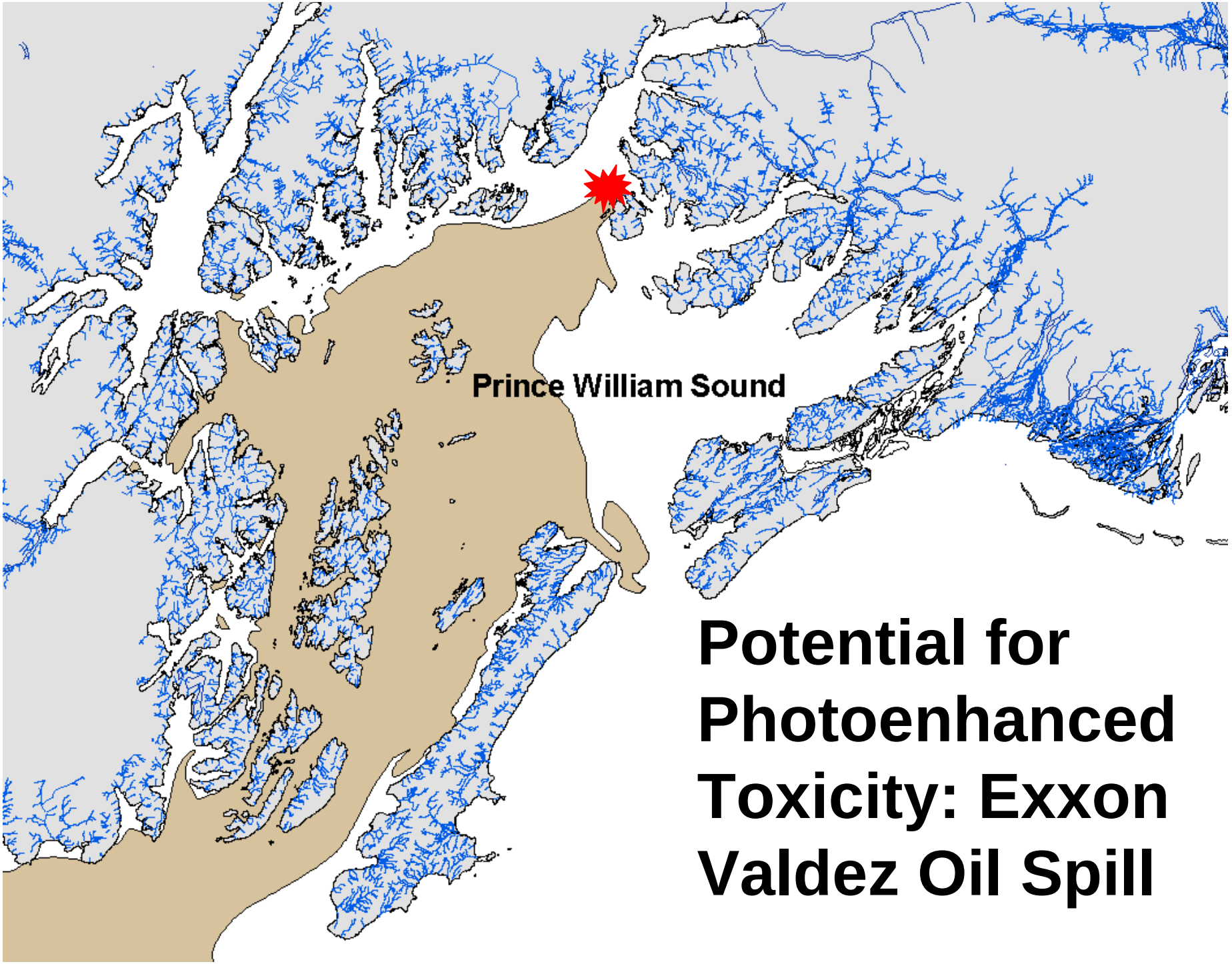
# UV Exposure

**Water column attenuation**

- colorous ocean water: >15 m
- turbid water, high DOC: < 0.5 meters
- subarctic Alaska: 0.1 to 8 m

**Aquatic organisms at risk**

- life stage, species-specific sensitivity
- demonstrated in over 30 species
- shallow water, intertidal habitats
- translucent eggs and larvae in photic zone



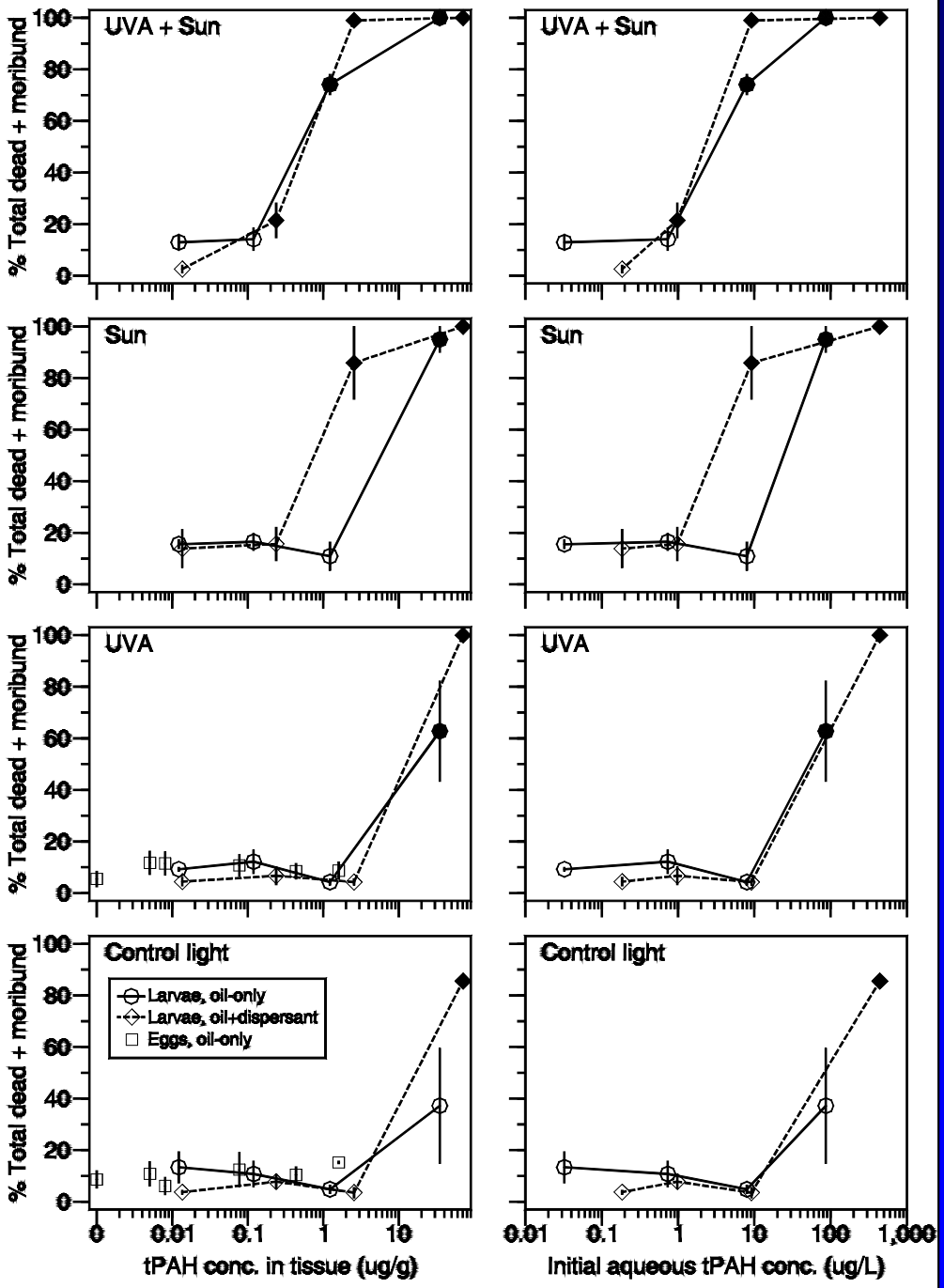

# Potential for Photoenhanced Toxicity: Exxon Valdez Oil Spill

# Sunlight Exposure

## Test Conditions


**Duration:**
**total 5 hr sunlight over 2 days**

**UV quant:**
**submersed radiometer in test vessel**



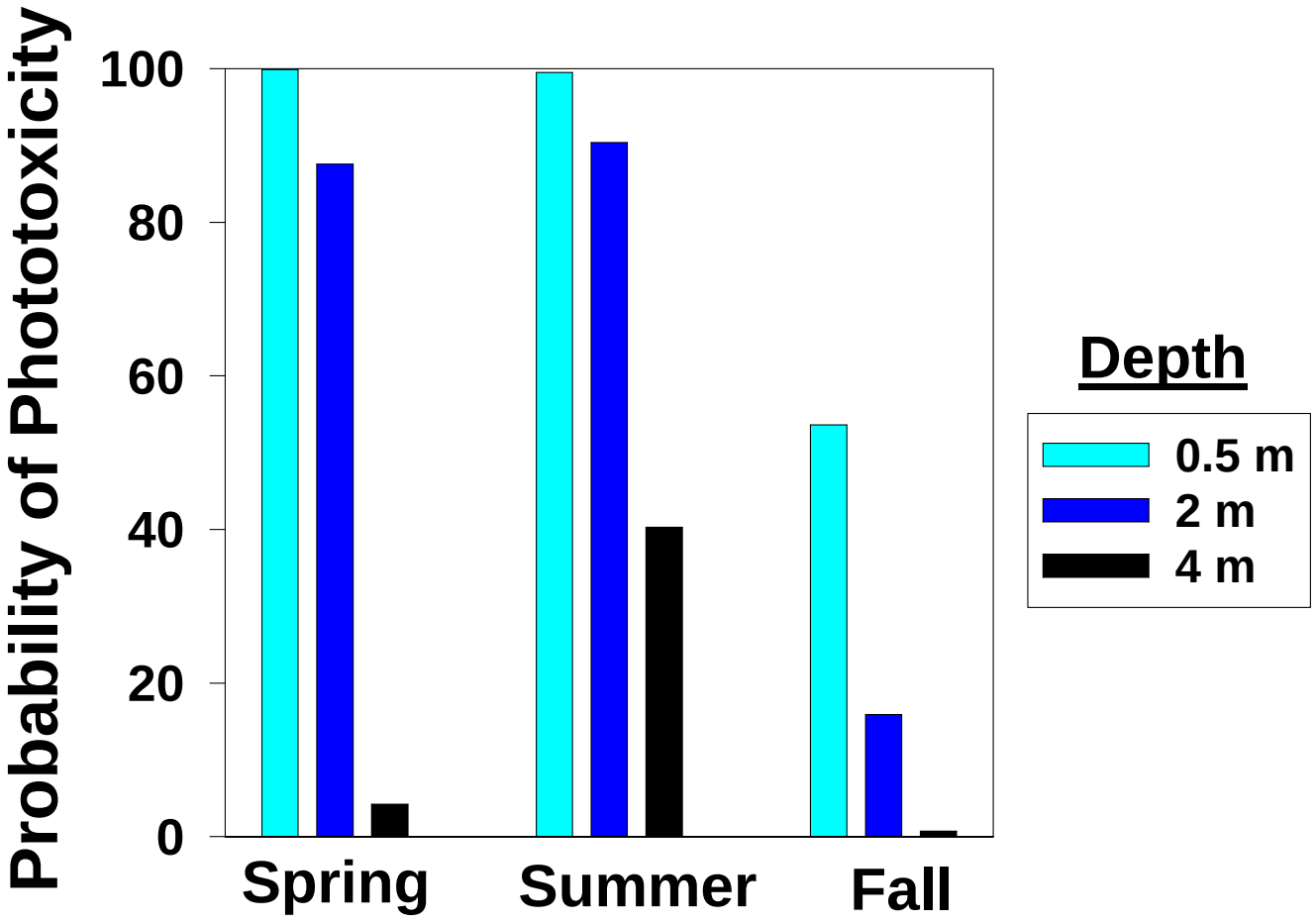

# Herring larvae

- Greater toxicity with increasing oil (tPAH) exposure
- Greater toxicity with increasing UV
- Toxicity more rapid with dispersant

# Risk Analysis

- calculate UVA doses in PWS water column from weekly surface UVA and season- location specific Kd
- derive phototoxicity threshold of 1 ug/L tPAH and 22 W*h/$m^2$ UVA threshold from herring larvae studies (Barron et al., 2003)
- determine if tPAH exceeded 1 ug/L during Exxon spill
- determine locations, seasons, depths that exceed UVA phototoxicity thresholds
- compute probability distributions of hazard quotients and probability of phototoxicity, based on 2003 UVA

# Phototoxicity Risks in Prince William Sound




Based on uncertainty, variability in surface UVA and Kd in PWS during 2003

# Results

- High probability of phototoxicity in PWS based on measured surface UVA and location-season specific Kd
- Risks were season, location, and depth specific
- High confidence in results:
  * temporally and spatial rigorous
  * risk probability based on UVA variability
  * ecologically relevant phototoxicity tests
  * same optics used in quantifying UVA dose in field and lab

# Conclusions

Phototoxicity demonstrated in over 20 different fresh and laboratory weathered and field collected oil products

Oils with phototoxic properties contain specific 3 ring to 5 ring phototoxic PAHs and heterocyclic aromatics

Demonstrated in over 30 species of aquatic organisms

Species at risk: translucent early life stages in photic zone; minimal pigmentation, armoring, refugia

Environmental phototoxicity requires sufficient oil and UV exposure
*requires bioaccumulation of PAH, heterocycles
*can occur at low ppb tPAH in water column; few hr sunlight exposure

# Recommendations

- Consider phototoxicity in spill response planning and impact assessment
- Determine seasonal and spatial risks from potential oil and UV exposure

# Questions?